Preparation of Fatty Acid Esters of Polyol Glucosides

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ABSTRACT

Starch is readily converted into glucosides by heating with a polyol, such as propylene glycol or glycerol, for a short time at 125 C in the presence of a catalytic amount of sulfuric acid. The product resulting from the reaction of 3 or more moles of polyol per anhydroglucose unit consists mostly of polyol monoglucosides, which are quite resistant to degradation under alkaline interesterification conditions. Attempts to interesterify the glucosides under the usual conditions employed with fats and oils (methyl esters, 0.1% sodium hydroxide, and temperatures up to 200 C) produced no glucoside esters. However, interesterification proceeded readily at temperatures between 160 and 200 C when 5 to 10% soaps and hydrophilic esters (mixtures containing mono- and diglycerides or an ester of diethylene glycol monomethyl ether) were employed. Under pressures low enough to rapidly distill off the freed polyol or alcohol, most reactions could be completed in less than an hour. Good yields of glucoside esters were obtained with starch, glycerol, and fat when the required operations were conducted in sequence in one vessel without intermediate purifications.

INTRODUCTION

Polyol glucosides can be prepared readily by the acid-catalyzed transglycosylation of starch and a polyol, such as glycerol, propylene glycol, or ethylene glycol (1,2). Esters of such glucosides and the long chain fatty acids should form a series of products having a number of uses. However, the preparation of such products would be expected to present some of the same problems encountered in the preparation of sucrose esters because polyol glucosides and fatty acid esters are immiscible.

The chemical literature contains only a few reports on the preparation and properties of polyol glucoside esters. Harries (3) described the reaction of a pyranoside sugar, such as glucose, with a polyol, such as glycerol, in the presence of an acid catalyst and the subsequent reaction of the resulting glycoside with a fatty acid in the presence of an esterification catalyst. Uses of the glycoside esters in breadmaking and margarine are suggested.

Myhre (4) describes a two-step process in which a sugar glycoside is first interesterified with a low molecular weight ester and the resulting product is then interesterified with a higher molecular weight ester to obtain a product claimed to be useful as an additive in cake mixes. Although the only examples given are for the preparation of methyl α-D-glucoside tetrapalmitate and methyl α-D-glucoside tetrabehenate, the process is claimed to be suitable for the preparation of a wide variety of glycoside esters. Data are presented to support the claim that the compounds are desirable additives for cake mixes.

Shvets et al. (5) have described the synthesis of glycosyl diglycerides.

Some polyol glucoside esters and closely related compounds occur naturally. Chloroplasts of photosynthesizing cells are known to have a large proportion of galactosyl diglycerides (6). Glycosyl diglycerides containing glucose, galactose, or mannose are widely distributed in Gram-positive bacteria (7). Carter et al. (8) isolated esters of glycerol galactosides from wheat flour, which now are recognized as being mostly galactosyl diglycerides and digalactosyl diglycerides. A diglycosyl diglyceride containing glucose (9) has been found among the glycolipids of rice bran.

The present investigation was undertaken to develop relatively simple procedures for making fatty acid esters of the polyol glucosides, primarily glycerol glucosides and propylene glycol glucosides.

EXPERIMENTAL PROCEDURES

The propylene glycol glucosides were prepared by a modification of the acid-catalyzed transglycosylation described by Otey et al. (10). Anhydrous propylene glycol (reagent grade) was placed in a round-bottom, three-neck reaction flask equipped with a glass-Teflon stirrer of the stuffing-box type, and the free space in the flask was flooded with dry nitrogen. After the propylene glycol was heated to 125 C, 0.33% concentrated sulfuric acid, calculated on the total weight of reactants to be used, was added. High amylose cornstarch (Mira-Quik C, A.E. Staley Manufacturing Company) from which ca. 13% moisture had been removed by drying at about 110 C was added over a period of 20 min in an amount equal to 1 anhydroglucose unit per 5 moles of propylene glycol. To keep the system anhydrous, the starch was added from a polyethylene bag attached to a standard taper joint inserted in one of the necks of the flask. After addition of the starch, the reaction was continued under an atmosphere of dry nitrogen for 60 min at 125 C. The reaction product was cooled to 90 C and the sulfuric acid was neutralized with sodium carbonate. Hot water was added and the solution was bleached with carbon (3%) and filtered through diatomaceous earth. The water and most of the free propylene glycol were removed by distillation and stripping with nitrogen at a reduced pressure, at temperatures up to 130 C. The dried glucosides were heated and mixed with 96% 2-propanol (1:4, w/w), cooled to -25 C overnight, and filtered. The propylene glycol glucosides in the filtrate, which contained over half of the total glucosides, were found to be composed of monoglucosides and to either contain barely detectable amounts or to be free of diglucosides, other oligosaccharides, and glucose. The filtrate glucosides, which were used in the interesterifications, did contain some propylene glycol. A small amount of water was added to the glucosides to facilitate handling. The propylene glycol and water were removed before each interesterification by stripping for 3 hr at 180 C with nitrogen at a reduced pressure.

Glycerol glucosides were prepared from the high amylose cornstarch by essentially the same procedure used to prepare the propylene glycol glucosides. However, 3 moles of glycerol per anhydroglucose unit were used in the transglycosylation. Fractionation of the glycerol glucosides was more involved. The neutralized reaction product was dispersed in anhydrous 2-propanol (1:4, w/w), and the fraction precipitating from solution between -25 C and -50 C was recovered. The insolubles at -25 C were extracted twice at 25 C with 94% 2-propanol (1:2, w/w), which dissolved glycerol monoglucosides. The glycerol glucosides used in the interesterifications were composited from several monoglucoside fractions, each of which was free of diglucosides, other oligosaccharides, and glucose. The glycerol glucosides

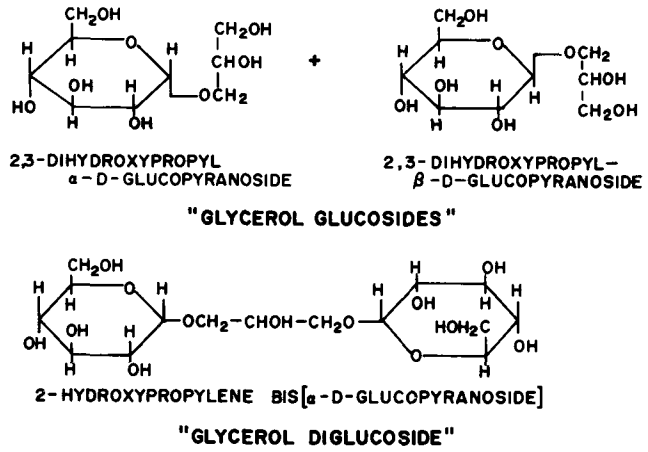

FIG. 1. Glycerol glucosides resulting from the reaction of starch and glycerol.

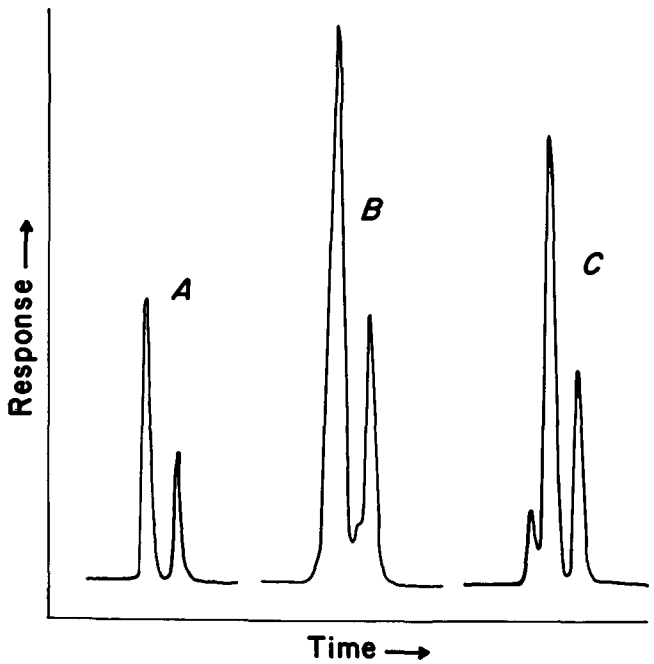

FIG. 2. Gas liquid chromatograms of silylated monoglucosides of ethylene glycol (A), propylene glycol (B), and glycerol (C).

were stripped at 200 C before being used.

The ethylene glycol glucosides were an experimental product prepared by Ashland Chemicals, Columbus, OH, using a modification of the procedure of Otey et al. (2). The product, which had a hydroxyl value of 1175 and which contained some di- and possibly higher glucosides, was received and used as a 71.5% solution in water.

The palmitic acid ester of 2-(2-methoxyethoxy–ethanol, or diethylene glycol monomethyl ether, was prepared by a stannous chloride-catalyzed esterification with a commercial palmitic acid (ca. 98% palmitic, 1% stearic, and 1% myristic). The excess of 2-(2-methoxyethoxy)ethanol used in the reaction was removed to a large extent by stripping at a high temperature and a low pressure. The crude ester was refined with alkali, bleached with clay, water washed, and dried.

Mixed palmitins were prepared by the stannous chloride-catalyzed esterification of glycerol and the commercial palmitic acid in a 2:3 mole ratio. The product after purification was found by gas liquid chromatography (GLC/ and thin layer chromatography (TLC) to have the following composition:

Component	Wt %
Monoglycerides	21.2
Diglycerides	59.3
Triglycerides	16.7
Free glycerol	1.3
Free fatty acids	1.0

The propylene glycol monoesters were a molecularly distilled product prepared from completely hydrogenated soybean oil by Distillation Products Industries, Rochester, NY.

The soaps used as catalysts were made in the laboratory from methyl esters by well-established procedures.

Interesterification Reactions

All interesterifications with the purified glucosides were condusted in a 50-ml, single-neck, round-bottom flask immersed in a silicone oil bath maintained at the temperature selected for the reaction. A Teflon-coated, magnetic stirring bar was used to mix the reactants; and a short, air-cooled condenser, bent to reduce refluxing to a minimum, was used to remove the by-product alcohol. The glucosides, freed of volatiles, and the fatty acid ester or esters (ca. 20 g total weight) were heated to the reaction temperature while under 1 atmosphere of nitrogen and while being mixed. Then the soap used as catalyst was added, and the pressure was reduced quickly and maintained at the selected level to distill off the freed alcohol or polyol. Taking the flask from the oil bath and cooling rapidly stopped the reaction. The reaction product, which usually was brittle and friable, was removed, ground to a powder, and analyzed.

Glycerol glucoside ester products were prepared from starch and each of several glycerides (cottonseed oil, fully hydrogenated cottonseed oil, coconut oil, and a mixture of mono-, di-, and tripalmitin) by a one-pot procedure. For each preparation 276.3 g (3 moles) anhydrous glycerol and 1.45 g (0.33%, based on the glycerol and starch to be used) of sulfuric acid were heated to 125 C under nitrogen in the glass reaction flask equipped with a mechanical stirrer. Anhydrous, high amylose cornstarch in the amount of 162.14 g (1 anhydroglucose unit) was added in the course of 20 min. The reaction was continued at 125 C for an additional 60 min. The resulting glycerol glucoside-glycerol solution was neutralized with sodium carbonate. The selected glycerides in the amount of 0.75 equivalent of fatty acids were added. Sodium soaps made from the glycerides employed were added in the amount of 5%, based on the weights of glycerol, glucosides, and glycerides.

With the reactants under nitrogen and the mechanical stirrer working, the temperature was raised to 190 C, and the reaction was continued for 20 min at atmospheric pressure. Glycerol then was removed by vacuum distillation for 80 min at 2-3 torr.

The crude reaction product was dispersed in a hot mixture of ethyl acetate and water containing 0.67 mole orthophosphoric acid per mole of soap. After the water layer was withdrawn, the ethyl acetate solution was washed first with a sodium chloride solution and finally with water.

Analysis

Gas liquid chromatographic analyses were made with an instrument (Aerograph Model 1520B, Varian Associates, Palo Alto, CA) equipped with flame ionization detectors and a 6-ft long, 0.125-in. stainless steel column packed with a silanized diatomaceous earth coated with 4% silicone gum rubber (SE-30, General Electric Co., Schenectady, NY). Column temperatures of 200-250 C were used, and some runs were temperature progremmed. The samples were silylated with a mixture of 1 part trimethylchlorowilane and 2 parts hexamethyldisilazane in anhydrous pyridine. Sucrose was used as an internal standard in quantitative analyses.

The polyol glycosides also were analyzed by TLC. The samples were spotted on silicic acid plates and developed with a solution of 2-propanol-ethyl acetate-water-toluene (20:10:5:4, v/v) (11). The chromatograms were visualized by spraying with a copper acetate-orthophosphoric acid solution and charring for 20 min at 175 C (12).

A similar TLC method was used for the polyol glycoside esters, except that the chromatograms were developed with a solution of toluene-ethyl acetate-95% ethanol (2:1:1, v/v) (11). Chromatograms of the glycerides and 2-(2-methoxyethoxy)ethyl palmitate on silicic acid plates were developed with a solution of petroleum ether-diethyl ether-glacial acetic acid (90:30:1, v/v) (13), and charred with the copper acetate reagent. Some of the chromatograms were quantified with the aid of a reflectance type densitometer.

RESULTS AND DISCUSSION

The glucosides resulting from the reaction of 3 moles glycerol with 1 anhydroglucose unit of starch consisted mostly of glycerol monoglucosides, namely, 2,3-dihydroxy-propyl-α-D-glucopyranoside and its β-anomer (Fig. 1). The mixture also contained glycerol diglucosides, such as 2-hydroxypropylene bis[α-D-glucopyranoside], and lesser amounts of higher glucosides. On the basis of TLC analyses, composition of the crude reaction products was unaffected by the type of starch used. In preliminary experiments, waxy cornstarch and purified amylose from potatoes yielded products identical with those obtained with the high amylose cornstarch.

Most of the experimental work was conducted with purified polyol glucosides consisting essentially of monoglucosides. Gas liquid chromatogrphic curves of the glucosides after silylation are reproduced in Figure 2. The peaks were related to specific compounds on the basis of published data (1,14).

In curve A, obtained with the ethylene glycol glucosides, the first and larger peak was produced by the α-glucoside and the second by its β-anomer. Curve B was obtained with the purified propylene glycol monoglucosides. In addition to the α- and β-anomer of the 2-hydroxypropyl compound, small amounts of the corresponding 1-hydroxypropyl compounds were formed and appeared as blips on the curve. Curve C was obtained with the purified glycerol monoglucosides. The largest peak was produced by 2,3-dihydroxypropyl-α-D-glucopyranoside, and the second largest peak was produced by its β-anomer. The smallest peak was attributed to 1,3-dihydroxypropyl-α-D-glucopyranoside. The peak for the β-form of the latter is believed to be hidden under one of the two larger peaks.

Thin layer chromatographic data on the crude reaction products and the purified monoglucoside fractions indicated that the purification procedures employed did not affect the ratio of the different monoglucosides present in a product. All products were free of glucose.

Attempts were made to interesterify polyol glucosides by procedures ordinarily used in making monoglycerides and rearranging fats. The mixtures were heated to 200 C in the presence of about 0.1% sodium hydroxide or a fraction of 1% soap. Several types of esters were employed, including methyl palmitate and 2-(2-methoxyethoxy)ethyl palmitate. No interesterification occurred.

The polyol glucosides could be readily interesterified when sizable proportions of both soap and hydrophilic esters were employed as intermediates. Under the most favorable conditions, at least 3% soap had to be used. No degradation of the polyol glucosides was observed at interesterification temperatures up to 220 C, which is in marked contrast to the behavior of sucrose under similar conditions (15).

Purified monoglucosides of propylene glycol were interesterified with 2-(2-methoxyethoxy)ethyl palmitate (mole ratio, 1:1) to obtain data on the effect of time and temperature (Fig. 3). A pressure of 5 torr was employed because this was sufficient to practically eliminate loss of 2-(2-methoxyethoxy)ethyl palmitate by distillation during the reaction. At 160 C and with 5% soaps, about half of the 2-(2-methoxyethoxy)ethyl palmitate reacted in 80 min. Doubling the amount of soaps forced the reaaction to practical completion in 80 min. These and other reaction curves obtained at 160 C are "S" shaped because the reactants did not form a homogeneous mixture in the early stages. At 200 C and 5% soaps the interesterification was about 80% completed in 10 min and practically completed in 20 min.

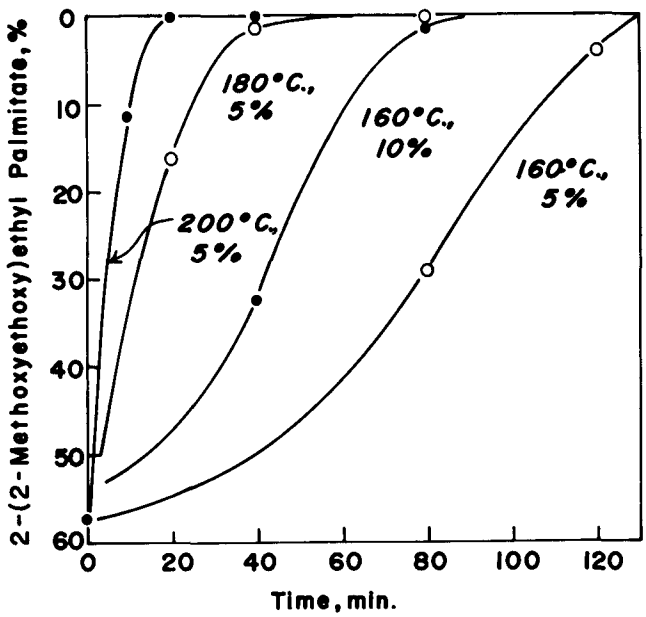

FIG. 3. Effect of time and temperature on the interesterification of propylene glycol monoglucosides and 2-(2-methoxyethoxy)ethyl palmitate (1:1 mole ratio) catalyzed with 5% and 10% soaps (mixture of 4 parts potassium palmitate and 1 part lithium palmitate).

In interesterifications like those represented in Figure 3, a mixture of potassium palmitate and lithium palmitate at a total of 5% produced a somewhat faster reaction rate than did potassium palmitate alone. When lithium palmitate was used alone, no interesterification occurred. Sodium palmitate was the most effective catalyst of all. With 5% sodium palmitate as catalyst, a temperature of 180 C and a pressure of 5 torr, 1 mole of 2-(2-methoxyethoxy)ethyl palmitate reacted completely with one mole of propylene glycol monoglucosides within 40 min.

To establish whether or not polyol glucosides were stable during interesterification, we reacted purified glycerol monoglucosides with mixed palmitins (0.75 equivalent of palmitic acid per mole of monoglucosides) for 80 min at 180 C and 2-3 torr. The catalyst was 4% potassium palmitate and 1% lithium palmitate. The unreacted glycerol monoglucosides were separated from the crude reaction product by washing with water containing exactly enough hydrochloric acid to decompose the soaps. The glycerol monoglucoside esters were subjected to a mild saponification in ethanol-water, and the freed glycerol monoglucosides were recovered after neutralization of the soaps. Examination of the glycerol monoglucosides before interesterification, the unreacted monoglucosides after interesterification, and the monoglucosides combined as palmitates revealed no evidence of degradation. However, it was found that the α-anomer interesterified more readily than did the β-anomer. Before interesterification, the ratio

TABLE I

Numbers of Isomers Possible on Acylating Glucosides and Sucrose with a Single Fatty Acid

Number of OH's esterified	Isomers		
	Propylene glycol glucoside[a]	Glycerol glucoside[a]	Sucrose
0	1	1	1
1	5	6	8
2	10	15	28
3	10	20	56
4	5	15	70
5	1	6	56
6	---	1	28
7	---	---	8
8	---	---	1

[a]Assuming only a single monoglucoside is present.

TABLE II

Glycerol Glucoside Ester Products Prepared by the One-Pot Method and Purified by Acidulation and Washing

Fat or oil used	Yield[a] (%)	OH value	Melting point (C)
Mist. of mono-, di-, and tri-palmitin	56.8	250	59
Coconut oil	64.3	384	ca. 26
Cottonseed oil	70.9	234	Glass
Fully hydrog. cottonseed oil	64.9	236	66

[a]Calculated on basis of crude reaction product remaining after interesterification under vacuum.

of α:β was 2.01:1. In the monoglucosides combined as esters, the ratio had increased to 2.40:1, but the ratio in the unesterified fraction had decreased to 1.55:1.

Partial acylation of polyol monoglucosides yields, of course, compounds of different levels of acylation and numbers of isomers for each level. The mole ratio of fatty acid to monoglucosides determines the acylation level of the esters formed in the largest proportions. Thus, for low ratios, mono- and diesters predominate.

In making products in which the lower esters predominated, no difficulty was encountered in obtaining homogeneous solutions during interesterification. However, when only 0.5 equivalent of palmitic acid in the form of mixed palmitins was interesterified with 1 mole of glycerol monoglucosides, somewhat more than 5% soaps was required to produce a homogeneous solution – 10% proved to be adequate.

Preparation of the higher esters was investigated. In one series of reactions, 2-(2-methoxyethoxy)ethyl palmitate was interesterified with propylene glycol monoglycosides at mole ratios of 3:1 and 5:1. Both reactions were conducted for 80 min at 200 C in the presence of 10% soaps (8% potassium palmitate plus 2% lithium palmitate). To avoid losing a significant amount of 2-(2-methoxyethoxy)ethyl palmitate by distillation, the relatively slow reaction at the higher ratio had to be conducted at 30 torr, instead of the usual 5 torr. At the 3:1 ratio the reaction went rapidly to completion, and the resulting product averaged 3 palmitoyl groups per molecule of propylene glycol glycoside palmitate. At the 5:1 ratio, 26% of the 2-(2-methoxyethoxy)ethyl palmitate remained unreacted after 80 min, and the molecules of propylene glycol monoglucoside palmitates averaged 4.4 palmitoyl groups.

An interesterification of mixed palmitins and glycerol monoglucosides, 6 equivalents of palmitic acid per mole monoglucosides, conducted at 220 C and 2-3 torr for 180 min, yielded a monoester-free product in which the glycerol monoglucoside palmitates averaged only 3.0 palmitoyl groups per molecule. In this reaction the mono- and dipalmitins were converted into relatively unreactive tripalmitin before the glycerol monoglucosides were substantially acylated.

The preparation of technical grade glycerol glucoside esters from cornstarch, glycerol, and a fat by the one-pot method presented no difficulties. The yields listed in Table II are based on the weight of crude product remaining after removal of free glycerol by vacuum distillation. The yields differ from each other mainly because the washing procedure employed also extracted some of the surface-active esters. Analyses of the crude reaction products indicated content of total esters over 70% in each case. Each of the washed products contained 75-80% glycerol glucoside esters, about 15% glycerides (mixture of mono-, di-, and triglycerides), and 6-9% free fatty acids. The hydroxyl values found are in the range of that for glycerol monoglucoside dipalmitate, which is 307.0. The monopalmitate has a hydroxyl value of 569.5 and the tripalmitate, 173.6.

The technical grade glycerol glucoside ester products could be made perfectly bland in flavor and odor. They were soluble in hexane and dispersed easily in water to form stable, milky emulsions. Each of the products was highly surface active. The product made with the mixed palmitates when added to cottonseed oil at a level of 0.04% lowered the interfacial tension to 1-3 dynes/cm. That for fottonseed oil and water alone was 29.4 dynes/cm.

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